

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet II.A4.89 R\_Oxygen4

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This data sheet last evaluated: June 2012; last change in preferred values: June 2012.



$$\Delta H^\circ = -149.6 \text{ kJ}\cdot\text{mol}^{-1}$$

### Low-pressure rate coefficients Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(7.5 \pm 2) \times 10^{-29} [\text{He}]$	295	Plumb and Ryan, 1981	DF-MS (a)
$7.5 \times 10^{-29} [\text{He}]$	298	Slagle et al., 1984	DF-MS (b)
$1.96 \times 10^{-5} T^{-8.24} \exp(-2150/T) [\text{He}]$	296-850	Wagner et al., 1990	PLP-MS (c)
$5.9 \times 10^{-29} [\text{He}]$	298		
<i>Relative Rate Coefficients</i>			
$(6.5 \times 2.0) \times 10^{-29} [\text{He}]$	298	Kaiser et al., 1990a	(d)

### Comments

- Measurements from  $2 \times 10^{16}$  to  $3.4 \times 10^{17}$  molecule  $\text{cm}^{-3}$  extrapolated to  $k_0$  and  $k_\infty$  with  $F_c = 0.85$ .
- Bath gas concentration varied between  $1.6 \times 10^{16}$  and  $2.4 \times 10^{17}$  molecule  $\text{cm}^{-3}$ . Data in agreement with values measured by Plumb and Ryan (1981).
- Experiments carried out in a heatable tubular reactor. He pressures from 0.7 to 20 mbar.
- $\text{C}_2\text{H}_5$  radicals were produced by UV irradiation of mixtures of  $\text{Cl}_2\text{-C}_2\text{H}_6\text{-O}_2$ . The consumed  $\text{C}_2\text{H}_6$  was determined by either FTIR or GC with flame ionization detection (which also allowed the amount of  $\text{C}_2\text{H}_5\text{Cl}$  formed to be measured). Rate coefficients were measured as a function of pressure (4 to 2000 mbar) relative to that of the reaction  $\text{C}_2\text{H}_5 + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{Cl}$ , and placed on an absolute basis by use of a rate coefficient of  $k(\text{C}_2\text{H}_5 + \text{Cl}_2) = 2.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 7 mbar.

### Preferred Values

$$k_0 = 5.9 \times 10^{-29} (T/300)^{-3.8} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 200 to 300 K.}$$

#### Comments on Preferred Values

We prefer the extensive data from Wagner et al. (1990) which were based on falloff extrapolations with modeled values of  $F_c = 0.64$  at 200 K and 0.54 at 300 K.

## High-pressure rate coefficients Rate coefficient data

$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(4.4 \pm 0.5) \times 10^{-12}$	295	Plumb and Ryan, 1981	DF-MS (a)
$4.4 \times 10^{-12}$	300	Slagle et al., 1984	DF-MS (b)
$1.3 \times 10^{-12} \exp(420/T)$	298-400	Munk et al., 1986	(c)
$5.3 \times 10^{-12}$	298		
$3.67 \times 10^{-14} T^{0.772} \exp(287/T)$	296-850	Wagner et al., 1990	PLP-MS (d)
$7.8 \times 10^{-12}$	298		
<i>Relative Rate Coefficients</i>			
$(9.2 \pm 0.9) \times 10^{-12}$	298	Kaiser et al., 1990b	(e)
$(8.1 \pm 0.3) \times 10^{-12}$	260-380	Kaiser, 1995	(f)
$2.9 \times 10^{-12} \exp(289/T)$	243-475	Dilger et al., 1996	(g)
$7.6 \times 10^{-12}$	298		

### Comments

- (a) See comment (a) for  $k_0$ .
- (b) See comment (b) for  $k_0$ .
- (c) Pulse radiolysis in  $\text{H}_2$  at 1 bar.  $\text{C}_2\text{H}_4$  radicals were generated from the reaction of  $\text{H} + \text{C}_2\text{H}_4$ .  $\text{C}_2\text{H}_5\text{O}_2$  radicals were monitored by absorption at 240 nm.
- (d) See comment (c) for  $k_0$ .
- (e) See comment (d) for  $k_0$ .
- (f) Photolysis of  $\text{Cl}_2$  in the presence of  $\text{C}_2\text{H}_6$ ,  $\text{O}_2$  and  $\text{M} = \text{He}$  or  $\text{N}_2$  at a pressure of 760 mbar.  $k$  was measured relative to the reaction  $\text{C}_2\text{H}_5 + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_5\text{Cl}_2 + \text{Cl}$  for which a rate coefficient of  $1.04 \times 10^{-11} \exp(300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  from Kaiser et al. (1990b) and Timonen and Gutman (1986) was employed.
- (g) Muon relaxation in longitudinal magnetic fields.  $\text{MuCH}_2\text{CH}_2$  radicals were generated by addition of muonium ( $\text{Mu} = \mu^+ \text{e}^-$ ) to  $\text{C}_2\text{H}_4$ . Total pressures of  $\text{N}_2$  varied between 1.5 and 60 bar.

### Preferred Values

$k_{\infty} = 7.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 200 K to 300 K.

#### *Comments on Preferred Values*

As for  $k_0$  we prefer the extensive data from Wagner et al. (1990). We assume a temperature independent rate coefficient  $k_{\infty}$  below 300 K. Falloff curves by Wagner et al. (1990) were fitted with an expression  $F_c = [0.58 \exp(-T/1250) + 0.42 \exp(-T/183)]$  which leads to an average value of  $F_c \approx 0.6$ . Within the stated error limits, the available data all agree with the preferred values.

The reaction competes with the chemical activation reaction  $\text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{HO}_2$  which becomes increasingly important with increasing temperatures. However, prompt  $\text{HO}_2$  yields from this reaction at 298 K and 1 bar of air are below 1 percent, see e.g. the analysis by Taatjes (2006), Clifford et al. (2000), Carstensen et al. (2005), and Miyoshi (2012) based on experiments from Wagner et al. (1990), Kaiser et al. (1990b), and Kaiser (1995).

### Preferred Values

Parameter	Value	T/K
$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$5.9 \times 10^{-29} [\text{N}_2]$	298
$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$5.9 \times 10^{-29} (T/300)^{-3.8} [\text{N}_2]$	200-300
$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$7.8 \times 10^{-12}$	298
$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$7.8 \times 10^{-12}$	200-300
$k(1 \text{ bar N}_2)/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$7.1 \times 10^{-12}$	298
$F_c$	0.6	200-300
<i>Reliability</i>		
$\Delta \log k_0$	$\pm 0.3$	298
$\Delta n_0$	$\pm 1.0$	200-300
$\Delta \log k_\infty$	$\pm 0.2$	298
$\Delta n_\infty$	$\pm 0.3$	200-300

The following text-line combines the preferred values for the high and low pressure limiting rate coefficients to generate a single, cut-and-paste expression for calculation of  $k$ :

$$=((5.9\text{e-}29*(T/300)^{-3.8}*M*(7.8\text{e-}12))/((5.9\text{e-}29*(T/300)^{-3.8}*M+(7.8\text{e-}12))*10^{(\log10(0.6)/(1+(\log10((5.9\text{e-}29*(T/300)^{-3.8}*M/(7.8\text{e-}12))/(0.75-1.27*\log10(0.6)))^2))})$$

The molecular density,  $M = 7.243 \times 10^{21} P(\text{bar})/T(\text{K})$

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